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(21) International Application Number: PCT/EP93/01773 (22) International Filing Date: 2 July 1993 (02.07.93) (30) Priority data: 9201226 8 July 1992 (08.07.92) NL (71) Applicant (for all designated States except US): NEDERLANDSE ORGANISATIE VOOR TOEGEPAST NATUURWETENSCHAPPELIJK ONDERZOEK (TNO) [NL/NL]; Schoemakerstraat 97, NL-2628 VK Delft (NL). (72) Inventor; and (75) Inventor/Applicant (for US only): TER MEULEN, Berend, Philippus [NL/NL]; Chamavenlaan 5, NL-7312 HE Apeldoorn (NL). (74) Agent: FLAMMAN, H.; Lioc Patents and Licensing B.V., P.O. Box 85096, NL-3508 AB Utrecht (NL).		(81) Designated States: JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: METHOD AND DEVICE FOR REGULATING THE HUMIDITY OF A GAS FLOW AND AT THE SAME TIME PURIFYNG IT OF UNDESIREO ACID OR ALKALINE GASSES (57) Abstract Method for regulating the humidity of a gas flow and at the same time purifying it of undesired acid or alkaline gasses. The gas flow is led across the retentive side of a membrane, through which water vapour can diffuse. A hygroscopic liquid flows on the permeation side of the membrane. A membrane is used, through which the acid or alkaline gasses concerned can diffuse. The hygroscopic liquid is mixed with a watery component of which the water content is adjusted to the desired humidity balance of the gas flow and the composition of which is adjusted to increasing and/or accelerating the solubility of the components in the mixture which are to be removed from the gas flow.		

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Method and device for regulating the humidity of a gas flow and at the same time purifying it of undesired acid or alkaline gasses.

The invention relates to a method for regulating the humidity of a gas flow and purifying that gas flow of, for example, acid or alkaline gasses, whereby the gas flow is led along a side - the retentive side - of a membrane, through which water vapour can diffuse and on the other
5 side of which - the permeation side - a hygroscopic liquid flows.

It is known how to remove water vapour from a gas flow by condensing the liquid therein by cooling it to under the dew point. In order to adjust the humidity of a gas flow to a particular desired value it is also possible to first warm up the gas, to saturate it with liquid
10 at that temperature, and to thereafter cool it to the desired dew point.

Other methods to remove water vapour from a gas are those, in which use is made of hygroscopic media or salts.

A practical and continuously usable method of this sort is described in US patent no. 4.915.838: in order to remove water vapour from
15 air, the air flow which is to be dried is led along the retentive side of a micro-porous membrane. The membrane which is used is a so-called hollow-fibre membrane.

A hygroscopic liquid flows on the permeation side of the membrane.
20 Water vapour from the gas flow diffuses through the pores of the membrane from the retentive side to the permeation side and is there absorbed and carried off by the hygroscopic liquid.

There is a wide area of application for the use of methods for regulating the humidity of gasses such as air: in buildings, means of
25 transport, etc.. It is especially often also important thereby to purify those gasses from undesired, for example dangerous, gas parts, such as the acid gasses H_2S , SO_2 , NO_2 , CO_2 , etc., but also of alkaline gasses such as NH_3 and others. As concerns the removal of dangerous gasses in air one can think of applications in the event of polluted
30 air in industrial and urban areas, alongside motorways, but also inside buildings and means of transport, such as, for example, in museums, in order to prevent damage to works of art as a result of penetrating gasses or tobacco smoke.

This removal of undesired parts from air cannot take place at the same time as the methods described above for regulating the humidity of that air. By, for example, cooling that air to below the dew point only the condensable parts can be removed therefrom, assuming then that the dew points of those parts correspond with one another. And if hydroscopic media are used, then except for water vapour this does not remove any other gas.

The invention relates to a method with which the regulation of the humidity of an air flow and the removal therefrom of undesired gasses, which are absorbed well in alkaline, acid or neutral watery solutions, can be achieved simultaneously in a single process. The method according to the invention is characterized to that end in that a membrane is used through which the gasses concerned which are to be removed can also diffuse and that the hydroscopic liquid is mixed with a watery component, in such a manner that the water content of the mixture is adjusted to the desired humidity balance of the gas flow which is to be treated and that the composition thereof is adjusted to the solubility therein of the, for example, acid and alkaline components which are to be removed from the gas flow.

The water content of the hydroscopic mixture is decisive for the humidity balance which is to be adjusted. As the membrane can allow water vapour to pass through in both directions - from the retentive side to the permeation side and vice-versa, water vapour can be both added to the gas flow which is to be treated and can be removed therefrom. And as a result of diffusion of the gas component(s) concerned from the retentive side of the membrane to the permeation side thereof, followed by absorption in the watery, possibly acid or alkaline component of the hydroscopic mixture which flows along the permeation side of the membrane, that (those) gas component(s) are removed from the gas flow which is to be treated simultaneously with the adjustment of the humidity. For that purpose the watery component must be of such a composition, that the solubility of the component which is to be removed is increased and/or is accelerated by a physical or chemical interaction. The composition must be adjusted to the nature of the gasses which are to be removed. For example, strong or weak organic or anorganic acids or alkalines are dissolved therein.

Good results are achieved with a hygroscopic liquid which consists of polar glycols, alcohols or glycerols such as triethyleneglycol or polyethyleneglycol or mixtures thereof. Watery electrolyte solutions with hygroscopic qualities are also possible. In general it applies, that such a hygroscopic mixture, the hygroscopic liquid with the parts dissolved therein, must be chosen which is compatible with the membrane and module materials which are to be used.

The invention also includes a method to regenerate a hygroscopic mixture used for regulating the humidity during the process until it has the desired water content again. That method is characterized to that end in that the mixture is then first heated or cooled to a certain temperature, it is then brought into contact via a membrane which is permeable for water vapour with a gas flow with a certain humidity, until equilibrium is reached and finally the mixture is cooled again, or respectively heated again, to the working temperature.

The membrane module which is to be used contains one or more membranes, which are micro-porous and hydrophobic. Polypropylene, for example, suffices in this respect. In any event, they must have a sufficiently large exchange surface for the purpose; they may be hollow-fibre membranes, but also flat membranes can be applied. In principle it makes no difference on which side of the membrane the gas, or the liquid flow respectively, are led. For example, in the case of a hollow-fibre membrane either the liquid flow or the gas flow can flow through the fibre.

Under certain circumstances it is preferable to use the said type of membrane with a non-porous top layer. Such membranes are especially advantageous if, as a result of the nature of the hygroscopic mixture and/or the manner in which the procedure is carried out, there is a chance of undesired passing-through of the hygroscopic mixture through the pores of the micro-porous membrane. A thin top layer consists, for example, of PDMS (silicon rubber) or polytrimethylsilylpropyne, or of thin gel layers on a polymer basis.

Naturally, the permeability of this top layer for both water vapour and for the parts which are to be removed from the gas which is to be treated must be sufficiently large in order to ensure that an effective removal is achieved. Such a top layer may be hydrophobic or hydro-

philic.

In the event of use of membranes with a non-porous top layer, there will be a preference, on the grounds of considerations with regard to an effective substance transfer, in the choice of the membrane side along which the liquid, or the gas, respectively, flows, for a flow of the liquid across the top layer. On the grounds of possible pollution from the gas/air phase, a choice may be made, however, for a flow of gas/air across the top layer: dirt will then stick before the top layer and will not penetrate the porous layer of the membrane.

The invention also includes a device for the implementation of the method described above. To that end it contains a membrane module with one or more membranes through which both water vapour and the, for example, acid or alkaline gasses, which are to be removed can diffuse, and equipped with means to lead the gas flow which is to be purified and regulated as concerns humidity across it on the one side of the membrane(s), and to lead an acid, alkaline or neutral hygroscopic mixture across it on the other side.

The membranes are then preferably micro-porous and hydrophobic, have a sufficiently large exchange surface and may be equipped with a non-porous top layer with a sufficiently large permeability for the substances which are to diffuse through it.

There now follow descriptions of several embodiments of methods according to the invention, in which the various aspects thereof are indicated.

In general it applies, that the concentration of the acid or the alkaline in the absorption liquid, or also in the total mixture, varies with the quantity of water which is removed from the air flow which is to be treated, or which is added thereto, as the case may be.

Example 1

A humid nitrogen flow with an SO₂ content of 500 ppm was lead at 20 °C with a flow rate of 4 liters per minute through the fibres of a hollow-fibre membrane module (type ENKA LM2P06), polypropylene fibres, microporous). The membrane module has fibres with an internal diameter of 0.6 mm and a total membrane surface of 400 cm². As absorption liquid the fibre bundle was surrounded on the outside by 0.25 l/min. of a mixture of ethylene glycol and sodium carbonate solution. The ratio of

ethylene glycol and sodium carbonate solution in this mixture was 4:1 on a weight basis. For the incoming nitrogen flow a relative humidity of approximately 94% was measured, with a dew point of 18.8 °C. The SO₂ concentration was brought to 500 ppm.

5 In the outgoing nitrogen flow a relative humidity of approximately 61% was measured, with a dew point of 12.1 °C. A content of 0.5 ppm was measured as SO₂ concentration of the outgoing nitrogen flow.

It therefore appears that at the same time the humidity of the nitrogen flow has been regulated, or has decreased, and the SO₂ content
10 of the nitrogen flow has been reduced by 99%.

Example 2

In the same membrane module as in example 1 a dry nitrogen flow was led through the fibres with an SO₂ content of 500 ppm, with a flow rate of 4 liters per minute. As absorption liquid a liquid was pumped
15 around the fibres, containing approximately 80% ethylene glycol and approximately 20% 1 M sodium carbonate solution. The absorption liquid had a flow rate of approximately 0.5 liters/min. The working temperature was approximately 28 °C.

In the incoming nitrogen flow a relative humidity of approximately
20 10% was measured, with a dew point of -5.5 °C.

In the outgoing nitrogen flow an SO₂ concentration of 0.5 ppm and a relative humidity of approximately 41% (dew point 14.0 °C) was measured.

It therefore appears, that at the same time the humidity of the
25 nitrogen flow has been regulated, or has increased, and the SO₂ content of the nitrogen flow has been reduced by 99%.

Example 3

In the same set-up as in examples 1 and 2 it was then investigated what influence the concentration of sodium carbonate has on the degree
30 of removal of SO₂ from the nitrogen flow. For this purpose the sodium carbonate solution was decreased from the original 1 Mol to 0.3 M and 0.1 M, respectively. It was found that at 0.3 M sodium carbonate the degree of removal for SO₂ was still 99% higher. At 0.1 M sodium carbonate it appeared that the degree of removal of SO had been reduced
35 to approximately 90%.

Example 4

In the same experimental set-up as in examples 1 and 2 it was then investigated what removal of SO₂ from the nitrogen flow can be achieved in mixtures of ethylene glycol and water (without sodium carbonate) and in water alone. The outgoing concentration of SO₂ in the nitrogen flow was hereby lowered to 51.3 ppm. Degrees of removal of a maximum of 50% were found; in the case of a longer duration of the experiment the degree of removal dropped to approximately 40% or lower. From the results of the examples 3 and 4 it can be deduced that without the addition of sodium carbonate, or with the addition of sodium carbonate in a concentration lower than 0.1 M, the degree of removal for SO₂ decreases quickly. It seems that the solution becomes rapidly saturated with SO₂ in that event, so that further absorption is obstructed. For an efficient removal of SO₂ and simultaneous regulation of the humidity of the nitrogen flow a sodium carbonate concentration of 0.1 M or higher is therefore necessary.

Example 5

In the same experimental set-up as in examples 1 and 2 the experiment of example 1 was repeated, but with the difference that a mixture of tri-ethylene glycol (TEG) and a potassium carbonate solution (1M) was used as an absorption liquid. The ratio of TEG and potassium carbonate solution in this mixture was approximately 4:1 on a weight basis. The same degree of removal for humidity, and at the same time for SO₂, was measured as in example 1.

The conclusion can be drawn that, with a mixture of TEG and potassium carbonate solution, the humidity for the nitrogen flow can be regulated, and at the same time the SO₂ content can be reduced by 99%, in the same manner as with the mixtures used in examples 1-4.

Claims

1. Method for regulating the humidity of a gas flow and purifying that gas flow of, for example, acid or alkaline gasses, whereby the gas flow is led across a side - the retentive side - of a membrane, through which water vapour can diffuse and on the other side of which - the permeation side - a hygroscopic liquid flows,

characterized in that a membrane is used, through which the acid or alkaline gasses concerned can diffuse and in that the hygroscopic liquid is mixed with a watery component, in such a manner that the water content of the mixture is adjusted to the desired humidity balance of the gas flow which is to be treated and the composition thereof is adjusted to the increase and/or acceleration of the solubility therein of the, for example, acid or alkaline components which are to be removed from the gas flow.

2. Method according to claim 1,
characterized in that the hygroscopic liquid consists of polar glycols, alcohols or glycerols, such as triethylene glycol or polyethylene glycol or mixtures thereof.

3. Method according to claim 1 or 2,
characterized in that the hygroscopic liquid consists of a watery electrolyte solution with hygroscopic qualities.

4. Method according to claim 1 - 3,
characterized in that during the implementation of the method the hygroscopic mixture which is used is regenerated until the desired water content is reached, by first heating it or cooling it to a particular temperature, then bringing it into contact, via a membrane which is permeable for water vapour, with a gas flow with a certain humidity, until equilibrium is reached, and finally cooling the mixture again or heating it to the working temperature.

5. Method according to one of the claims 1 - 4,
characterized in that a membrane module is used with one or more microporous, hydrophobic membranes, with a sufficiently large membrane exchange surface.

6. Method according to claim 5,
characterized in that a membrane/membranes is/are used with a non-porous top layer, which has a sufficiently large permeability for both

water vapour and for the, for example, acid or alkaline gasses which are to be removed.

7. Device for implementing one of the methods according to claims 1 - 6, containing a membrane module with one or more membranes through which both water vapour and the, for example, acid or alkaline gasses which are to be removed, can diffuse, and equipped with means to lead the gas flow which is to be purified and regulated as concerns humidity across it on the one side of the membrane/membranes, and to lead an acid, alkaline or neutral hygroscopic mixture across it on the other side.

8. Device according to claim 7,
characterized in that the membrane/membranes is/are (a) micro-porous hollow-fibre membrane(s), made from hydrophobic materials.

9. Device according to claim 7,
characterized in that the membrane/membranes is/are flat, micro-porous and hydrophobic with a sufficiently large membrane exchange surface.

10. Device according to one of the claims 7, 8 and 9,
characterized in that the membrane/membranes is/are equipped with a non-porous top layer, with such a permeability for water vapour and the acid or alkaline gasses, that the method according to claim 6 can be implemented.

INTERNATIONAL SEARCH REPORT

Intern. Appl. No.

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 B01D53/26 B01D53/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 147 754 (WILLIAM J. WARD) 3 April 1979 ---	
A	US,A,4 900 448 (ULRICH BONNE) 13 February 1990 ---	
A	WO,A,91 15284 (T.N.O.) 17 October 1991 ---	
A	US,A,5 084 073 (RAVI PRASAD) 28 January 1992 ---	
A	EP,A,0 308 002 (T.N.O.) 22 March 1989 ---	
A	EP,A,0 430 331 (T.N.O.) 5 June 1991 -----	

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Further documents are listed in the continuation of box C.

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Patent family members are listed in annex.

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Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4147754	03-04-79	NONE	
US-A-4900448	13-02-90	US-A- 4915838	10-04-90
WO-A-9115284	17-10-91	NL-A- 9000783 EP-A- 0524242	01-11-91 27-01-93
US-A-5084073	28-01-92	CN-A- 1060417 EP-A- 0481363 JP-A- 4265111	22-04-92 22-04-92 21-09-92
EP-A-0308002	22-03-89	NL-A- 8702150 DE-A- 3870119 JP-A- 1159025 US-A- 4913818	03-04-89 21-05-92 22-06-89 03-04-90
EP-A-0430331	05-06-91	NL-A- 8902897 JP-A- 3181310	17-06-91 07-08-91